Phase directed excitonic transport and its limitations due to environmental influence

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We investigate theoretically the transfer of excitation along a one dimensional chain of monomers for a situation in which initially the excitation is shared coherently by two monomers. We show that depending on the relative phase between the two monomers strong directionality of the energy transfer is possible. It is also investigated how dephasing, induced by an environment, influences this directed transport.

I. INTRODUCTION

Controlling the direction of motion of a quantum mechanical wave packed has received much interest, e.g. in the context of unidirectional rotational motion[1–3]. In the present work we will investigate unidirectional excitation transfer in assemblies of monomers that interact via resonant dipole-dipole interaction (see for instance Refs.[4–13]). Among the various examples are molecular aggregates[14], organic molecular solids[15], light harvesting systems[16], chains of quantum dots, or chains of ultra-cold Rydberg atoms[17–19]. In all these systems the transport of electronic excitation can adequately be described by the exciton theory of Frenkel[20–22], where electronic excitation localized on a monomer can be transferred to another monomer due to transition dipole-dipole interaction.

In most of the studies of this excitation transfer usually the initial condition is taken in such a way that the excitation is localized on a *single* monomer, i.e. one monomer is electronically excited and all the others are in their electronic ground state (e.g. in Refs.[4,13,23–25]) Very little attention is paid to the investigation of initial states that extend over several monomers. In this situation, initial phase relations between different monomers play an important role[26]. With the increasing capability to create artificial structures, controlling the initial condition can be used to tailor the properties of such systems. One possibility to create a state where excitation is distributed coherently over several monomers, is to use electromagnetic radiation that has a definite phase relation between different monomers. Since for a typical molecular aggregate[14,16,27] the distance between the monomers is in the oder of a few Ångström and the excitation wavelength is in the visible, direct addressing of individual chromophores is quite difficult and would probably require the use of near-field methods. For chains of ultra-cold Rydberg atoms, where the distances between the monomers can be in the μm range[28,29], this addressing should be easier to achiv and in principle be possible with present-day technology.

In this work it is pointed out that, even for an initial state in which the excitation is delocalized only over two neighboring monomers, it is possible to obtain very strong unidirectional transport along a one-dimensional chain by a suitable choice of the relative phase between the excitations of neighboring monomers. To investigate the robustness of the directionality against fluctuations of the surroundings we describe the interaction of the Frenkel exciton with its environment within the Haken-Reineker-Strobl model, including pure dephasing.

The paper is organized as follows: In section II we specify the system considered and the initial states. In section III numerical calculations are performed to illustrate the influence of the relative phase on the direction of transport. Here also the interplay with the environment is investigated. In section IV we give intuitive analytical explanations for the observed directionality. In particular, an exact formula for the time-dependent mean-position of the excitation is derived, including the interaction with the environment. In section V we conclude with a summary of our findings and give a brief outlook.

II. DESCRIPTION OF THE SYSTEM

We consider a one dimensional array of N monomers. The monomers are described by electronic two-level systems, where $|\phi_n^g\rangle$ denotes the ground state and $|\phi_n^e\rangle$ the excited state of monomer n. The energy difference between the two states is denoted by ϵ_n. Since we focus on the transport of a single excitation, only aggregate stats of the form

$$|\pi_n\rangle = |\phi_1^g\rangle \cdots |\phi_n^e\rangle \cdots |\phi_N^g\rangle, \qquad (1)$$

where monomer n is excited and all the others are in their ground state, are taken into account. The aggregate is described by the Hamiltonian

$$H = \sum_{n=1}^{N} \epsilon_n |\pi_n\rangle\langle\pi_n| + \sum_{\substack{n,m=1 \\ n \neq m}}^{N} V_{nm} |\pi_n\rangle\langle\pi_m| \qquad (2)$$

corresponding to a simple Frenkel exciton model[16,30]. The transfer matrix element V_{nm} is typically taken to be of dipole-dipole form with a distance dependence $V_{nm} \sim 1/|R_n - R_m|^3$, where R_n and R_m are the positions of monomer n and m. We focus on a one-dimensional regular chain of equidistantly spaced monomers and use

$$V_{nm} = V \frac{1}{|n-m|^3}, \qquad n \neq m \qquad (3)$$

where V scales the interaction strength between the monomers. In the following we take $\epsilon_n = \epsilon$ independent of the monomer index n.

Following the approach of Haken, Reineker and Strobl[9,10], the interaction of the monomers with the surroundings is taken into account by the time dependent Hamiltonian

$$H'(t) = \sum_n q_n(t) |\pi_n\rangle\langle\pi_n| \qquad (4)$$

Here $q_n(t)$ are stochastic environment fluctuations which couple to the excitation on monomer n. They are taken to be real Gaussian random variables with mean

$$\langle q_n(t)\rangle = 0 \qquad (5)$$

and variance

$$\langle q_n(t) q_m(s)\rangle = \gamma_n \delta_{nm}\delta(t-s) \qquad (6)$$

The average over the fluctuations is denoted by $\langle\cdots\rangle$. In Eq. (6) we have assumed that fluctuations at different monomers n and m are uncorrelated and that the environment has no memory, i.e. it is Markovian. In recent years there has been much interest in the influence of non-Markovian environments on energy transfer[25,31] but to discuss the basic influence of the environment on the directed transport, a Markovian description will be sufficient. In the conclusions we will briefly discuss the effects of non-Markovian environments together with the influence of internal vibrations of the monomers. Furthermore we will assume that the γ_n are site independent, i.e. $\gamma_n = \gamma$ for all n.

From the Liouville–von Neumann equation, averaged over the environmental fluctuations, one finds for the matrix elements $\rho_{nm} = \langle\pi_n|\rho|\pi_m\rangle$ of the averaged density matrix[9]

$$\dot{\rho}_{nm}(t) = -\frac{i}{\hbar}[H,\rho(t)]_{nm} - \gamma\,(1-\delta_{nm})\rho_{nm}(t). \qquad (7)$$

The probability to find excitation on monomer n is given by the population $\rho_{nn}(t)$.

In the following, for convenience, we take the number of monomers N to be even and assume that initially the excitation is located on the two monomers in the middle of the chain, i.e.

$$\begin{aligned}
\rho_{N/2,N/2}^{\text{ini}} &= \rho_L \\
\rho_{N/2+1,N/2+1}^{\text{ini}} &= \rho_R \\
\rho_{N/2,N/2+1}^{\text{ini}} &= \rho_{LR} \\
\rho_{N/2+1,N/2}^{\text{ini}} &= \rho_{LR}^*
\end{aligned} \qquad (8)$$

where ρ_L denotes the population on monomer $N/2$ and ρ_R that on monomer $N/2 + 1$. The coherence between the two monomers is denoted by ρ_{LR}. All other elements are zero. In matrix notation this can be written as

$$\rho^{\text{ini}} = \begin{pmatrix} \mathbf{0} & \cdots & \cdots & \mathbf{0} \\ \vdots & \rho_L & \rho_{LR} & \vdots \\ \vdots & \rho_{LR}^* & \rho_R & \vdots \\ \mathbf{0} & \cdots & \cdots & \mathbf{0} \end{pmatrix} \qquad (9)$$

We take the initial population on monomer $N/2$ and $N/2+1$ to be equal, i.e. $\rho_L = \rho_R = 1/2$. Furthermore we write for the coherence $\rho_{LR} = a\exp(-i\Theta)$, with $a \geq 0$ and $-\pi < \Theta \leq \pi$. Of particular interest will be the phase factor Θ between the two monomers. For a pure initial state we have $a = 1/2$ and the corresponding initial wave function is given by

$$|\psi^{\text{ini}}\rangle = \frac{1}{\sqrt{2}}\left(|\pi_{\frac{N}{2}}\rangle + e^{i\Theta}|\pi_{\frac{N}{2}+1}\rangle\right). \qquad (10)$$

In the following we show how the phase factor Θ determines the directionality of excitation transfer.

III. NUMERICAL CALCULATIONS

In this section we will investigate numerically the time development of the populations $\rho_{nn}(t)$ by solving Eq. (7) for different values of the relative phase Θ and the dephasing rate γ. We take the interaction strength $|V|$ as unit of energy. Consequently we express time in units of $\hbar/|V|$ and the dephasing rate γ in units of $|V|/\hbar$.

Exemplarily, in Fig. 1 the transfer dynamics is shown for five values of Θ and two different γ for a chain of $N = 60$ monomers. The coupling V is taken to be positive (changing the sign of V leads to a reversal of the direction of propagation). Initially the excitation is localized on the sites 30 and 31 with a pure initial state as given in Eq. (10). In the left column the fully coherent case $\gamma = 0$ is shown. In the right column the case $\gamma = 0.3$ is shown. In each panel the time dependence of the mean

$$M(t) = \sum_n n\rho_{nn}(t) \qquad (11)$$

is displayed as a black solid line.

Consider first Fig. 1 c) and h) where $\Theta = 0$. Here one clearly sees a symmetric spreading of the initially localized excitation. The mean stays constant at its initial location. This case is similar to the situation where the excitation is initially localized only on one site (see e.g. Ref.[25]).

Upon increasing the phase difference Θ to positive values the transfer to the left becomes enhanced (while the transfer to the right decreases). For a value $\Theta = +\pi/4$ (see Fig. 1 b,g) already a clear asymmetry can be seen, which becomes stronger when increasing Θ. For $\Theta = \pi/2$ the transfer to the left reaches its maximum (see Fig. 1 a,f).
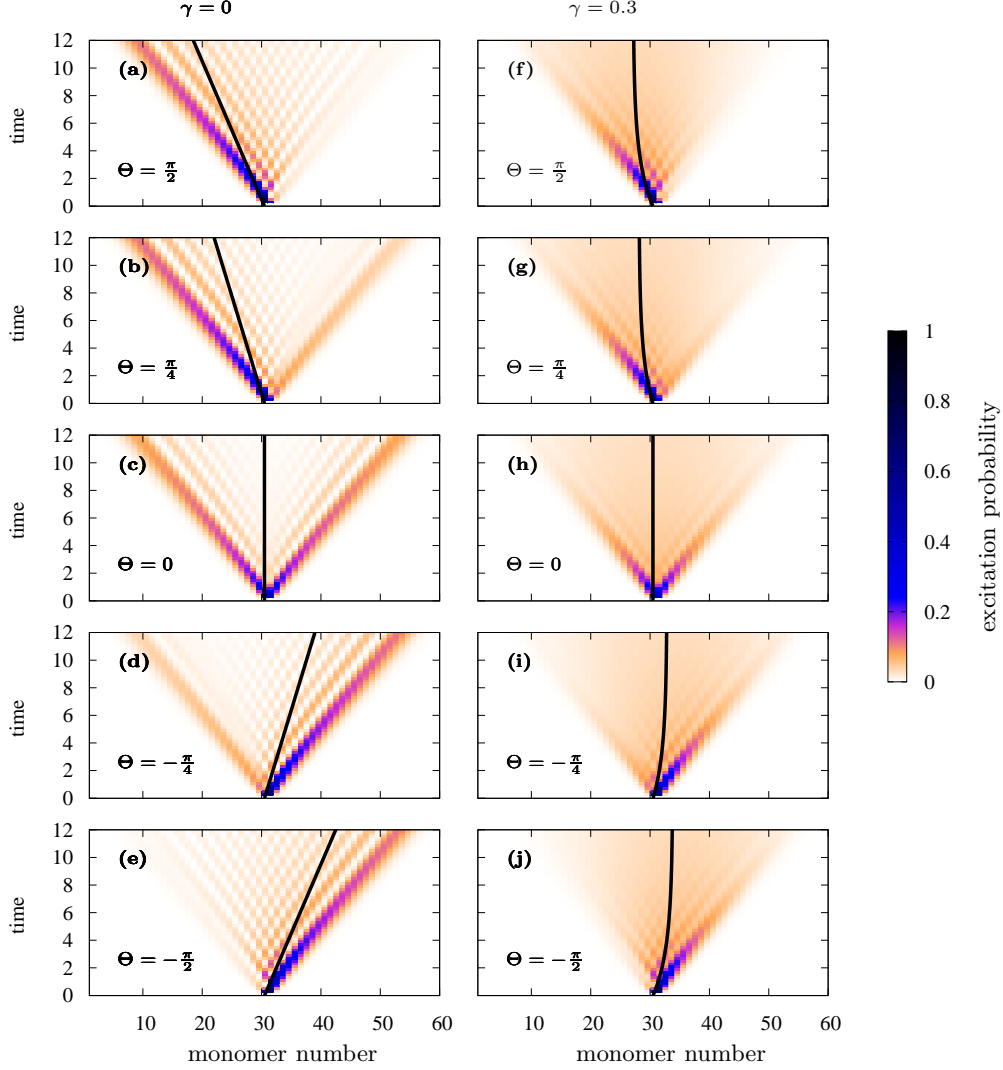
FIG. 1: Probability $\rho_{nn}(t)$ to find excitation on monomer n at time t for different values of the phase Θ and the dephasing rate γ. The black solid line is the time-dependent mean of the distribution $\rho_{nn}(t)$. Left column $\gamma = 0$, right column $\gamma = 0.3$. Time in units of $\hbar/V$. The values of Θ are indicated in the figures.

We have here restricted the discussion to the interval $-\pi/2 \leq \Theta \leq \pi/2$. The result for an arbitrary phase Θ can be simply related to the interval $[0, \pi/2]$. For example, for $\Theta > \pi/2$ we can write $\Theta = \pi/2 + \Theta'$ and we find the same result as for $\Theta = \pi/2 - \Theta'$. Note that a change of sign of Θ just reverses the directions. See Fig. 1 (d,i) for $\Theta = -\pi/4$ and Fig. 1 (e,j) for $\Theta = -\pi/2$.

While for the case $\gamma = 0$ (left column of Fig. 1) the excitation propagates as a well defined "wavefront" over the whole time-range of the propagation, in the case $\gamma = 0.3$ (right column) the exciton dynamics soon becomes similar to a diffusion process. This behavior is also reflected in the dynamics of the mean. First we note that one clearly sees the change of directionality with changing phase Θ. For the case $\gamma = 0$ the mean moves along the chain with constant velocity (characterized by the constant slope of the black line). This velocity depends on Θ. For a finite dephasing $\gamma = 0.3$ and short times the mean also moves with the same velocity as in the case $\gamma = 0$. Soon, however, it slows down and remains finally quasi constant. We will quantify these observations in the next section.

The strong dependence on the phase Θ can be seen even better by considering the probability to find excitation on the left or right side of the chain, i.e. by considering the quantities

$$P_L(t) = \sum_{n=1}^{N/2} \rho_{nn} \quad \text{and} \quad P_R(t) = \sum_{n=\frac{N}{2}+1}^{N} \rho_{nn}. \quad (12)$$
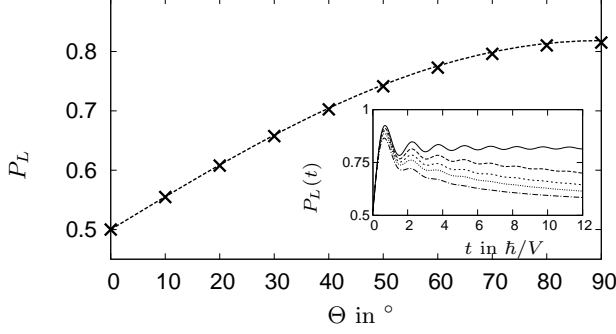
FIG. 2: Asymptotic population on the left side of the chain as a function of the initial phase Θ for the case of vanishing dephasing, i.e. $\gamma = 0$. Crosses are the numerical results for $t = 12\hbar/V$, the dashed line is the analytical solution Eq. (20). The inset shows the population $P_L(t)$ as a function of time for the initial phase $\Theta = \pi/2$ and different values of the dephasing rate γ. From top to bottom the values are $\gamma = 0.0,\ 0.1,\ 0.2,\ 0.3$ and 0.5.

In Fig. 2 the probability $P_L(t=12)$ (i.e. to have population on the left side at the final time $t = 12$ of Fig. 1), is shown as a function of the initial phase Θ. With increasing Θ initially there is a fast increase in P_L followed by a quite flat region around the optimum at $\Theta = \pi/2 = 90°$, thus for small deviations $\Delta\Theta \lesssim 20°$ from this optimum there is still nearly the optimal directionality. The inset shows the population $P_L(t)$ as a function of time for the initial phase $\Theta = \pi/2$ and different values of the dephasing rate γ.

IV. ANALYTICAL CONSIDERATIONS

A. The fully coherent case

In this section we give an intuitive explanation for the observed directed transport. Since the important contribution to directionality stems from the coherent motion of the excitation, in the following we will focus on the case $\gamma = 0$. To obtain simple analytical results we restrict to nearest neighbor interaction and impose periodic boundary conditions (i.e. $V_{N,1} = V$). Then the eigenstates of Eq. (2) are given by[16]

$$| \phi_k \rangle = \frac{1}{\sqrt{N}} \sum_{n=1}^{N} e^{ikn} | \pi_n \rangle \qquad (13)$$

with

$$k = \frac{2\pi}{N} j, \quad j = -N/2, \ldots, N/2 - 1. \qquad (14)$$

The corresponding eigenenergies are

$$E_k = \epsilon + 2V \cos k. \qquad (15)$$

With these results we will now discuss how one can understand directionality from the initial population of eigenstates $| \phi_k \rangle$. The sign of the wave vector k appearing in the definition of the eigenstates and eigenenergies can be viewed as the direction of propagation associated with the stationary state Eq. (13)[20]. For $N \to \infty$ the mean velocity associated with the wave vector k is given by $v_k = \partial_k E(k) = -2V \sin(k)$. For instance for $k > 0$ and positive V the velocity is directed to the left. Expanding the initial state $| \psi^{\text{ini}} \rangle$ defined in Eq. (10) w.r.t. the basis states Eq. (13) one finds

$$| \psi^{\text{ini}} \rangle = \frac{1}{\sqrt{2N}} \sum_k e^{-ikN/2} \big(1 + e^{i(\Theta - k)} \big) | \phi_k \rangle. \qquad (16)$$

The probability to find a certain k within the initial state $| \psi^{\text{ini}} \rangle$ (defined in Eq. (10)) is given by

$$P_k = |\langle \phi_k | \psi^{\text{ini}} \rangle|^2 = \frac{1}{N} \big(1 + \cos(k - \Theta) \big). \qquad (17)$$

From this equation one sees that for $\Theta = 0$ the probability to find positive and negative k-values is equal. For negative values of Θ the maximum of the function P_k is shifted to positive k, i.e. velocities directed to the right for $V > 0$. This has consequences also for the initial velocity

$$v^{\text{ini}} = \sum_k P_k v_k = -V \sin(\Theta), \qquad (18)$$

which shows a sinusoidal dependence on the phase Θ. We will come back to this result in the next section.

Consider now the probability to find positive k-values in the initial state

$$P_{k>0} = \sum_{j=1}^{N/2-1} P_{\frac{2\pi}{N}j} = \frac{1}{2} - \frac{1}{N} + \frac{\cot\left(\frac{\pi}{N}\right)}{N} \sin(\Theta). \qquad (19)$$

In the limit $N \to \infty$ Eq. (19) simplifies to

$$P_{k>0} \approx \frac{1}{2} + \frac{\sin(\Theta)}{\pi} \qquad (20)$$

This analytical function is shown in Fig. 2 as a dashed line. It is in very good agreement with the asymptotic populations (crosses in Fig. 2) found numerically for the case $\gamma = 0$. Thus $P_{k>0}$ is just the population on the left side of the chain at large times, i.e. $P_L(t \to \infty) = P_{k>0}$. For a finite chain this result holds only for times before the first reflection at the end of the chain occurs. Note that the time has to be large enough so that the initial oscillations shown in the inset of Fig. 2 do not play a role anymore.

B. The first moment of exciton motion

As seen in Section III the mean position of the excitation $M(t)$, defined in Eq. (11), is a useful measure to

quantify directionality. For our initial condition the excitation is localized on monomer $N/2$ and $N/2 + 1$ with equal probability. Thus, $M(t) > (N+1)/2$ means that the excitation is mainly localized on the right side of the chain, for $M(t) < (N+1)/2$ it can mainly be found on the left.

Following the treatment of Reineker[32] we can find a differential equation for $M(t)$. In the following, for simplicity, we assume nearest neighbor interactions only and write $V_{nm} = V(\delta_{m,n+1} + \delta_{m,n-1})$ with equal interaction between all neighboring monomers. Furthermore we consider an infinite chain. Then, after some algebra, one finds

$$\frac{d}{dt}M(t) = V \cdot \phi(t) \tag{21}$$

with

$$\phi(t) = i \sum_n (\rho_{n+1,n} - \rho_{n,n+1}) \tag{22}$$

Differentiating $\phi(t)$ w.r.t. time and noting that $\sum_n \rho_{nn} = \sum_n \rho_{n+1,n+1}$ and $\sum_n \rho_{n+2,n} = \sum_n \rho_{n+1,n-1}$, from Eqs. (7) and (22) we get

$$\frac{d}{dt}\phi(t) = -\gamma\phi(t). \tag{23}$$

This equation can be easily integrated to give

$$\phi(t) = \phi(0)e^{-\gamma t} \tag{24}$$

with $\phi(0)$ determined by the initial density matrix ρ^{ini}. Note that for our special initial condition Eq. (8) with $\rho_{LR} = a \exp(-i\Theta)$ one has $\phi(0) = 2\,\text{Im}\rho_{LR} = -2\,a\sin\Theta$. Inserting the result Eq. (24) into Eq. (21) gives

$$M(t) = M(0) + \begin{cases} V\phi(0) \cdot t & \text{for } \gamma = 0 \\ \frac{V}{\gamma}\phi(0)(1 - e^{-\gamma t}) & \text{for } \gamma \neq 0 \end{cases} \tag{25}$$

From Eq. (25) one sees that the initial density matrix ρ^{ini} (entering via $\phi(0)$) plays a crucial role in the time evolution of $M(t)$. If $V\phi(0) > 0$ the mean $M(t)$ will move to larger n. Note that a change of the sign of V also changes the direction.

Before considering the initial condition Eq. (8) in more detail, let us first discuss the dependence on the dephasing rate γ. From Eq. (25) one sees that for $\gamma = 0$ the mean $M(t)$ moves with a constant velocity given by $|V\phi(0)|$, which for a pure state (where $\phi(0) = -\sin\Theta$) is in agreement with Eq. (18) obtained by considering the distribution of k-values in the initial state. For $\gamma \neq 0$ this velocity becomes time-dependent. As long as $t \ll 1/\gamma$ one can expand Eq. (25) to find $M(t) \approx M(0) + V\phi(0)t + \ldots$. Thus initially the mean moves with the same velocity as without dephasing. For $t \gtrsim 1/\gamma$ the directionality of the transfer is mostly lost and the mean $M(t)$ slowly approaches its long time limit

$$M(t \gg 1/\gamma) = M(0) + \frac{V}{\gamma}\phi(0) \tag{26}$$

After this discussion of some general properties of $M(t)$ we go back to the special initial condition Eq. (8) with $\rho_{LR} = a\exp(-i\Theta)$. Then, as already noted above, one has $\phi(0) = -2\,a\sin\Theta$. For given V and a the direction of transport is solely determined by the phase Θ. We find that for $\Theta < 0$ the transport is directed to the right (for positive a and V) with maximum at $-\pi/2$ while for $0 < \Theta < \pi$ it is directed to the left. For $\Theta = 0$ the situation is symmetric and the mean remains $M(0)$. Note that a scales the "strength" of directionality. For a fully mixed state ($a = 0$) there is no directionality; for a pure initial state ($a = 1/2$) the directionality is maximal.

V. SUMMARY AND CONCLUSIONS

In the present work we have investigated how the direction of excitation transfer along a one-dimensional aggregate depends on the relative phase between two initially excited monomers. It was found that in the case, when there is no interaction with the environment, for a phase difference of $\pi/2$ more than 80% of the excitation propagates into one direction. The direction depends on the sign of the phase. For smaller phase differences the directionality decreases. The same holds, if the initial state is not pure. As expected interaction with an environment, which destroys phase relations between excitations on different monomers, leads to a strong decrease of the directionality. In this case, the directionality of the propagating wave-packet is only conserved on timescales of the order of the dephasing time. This dependence on the initial phase is also reflected in the time-dependence of the mean of the excitation. For this quantity exact analytical results have been derived, showing in particular that initially the velocity of the mean is given by the product of the transfer-interaction between the monomers and the sine of the phase-difference in the initial state. In the fully coherent case this velocity remains constant; with dephasing the velocity decreases exponentially on the timescale of the dephasing time. While fluctuations of the environment can often be helpful to enhance the transport efficiency of excitonic energy[12,33], in the present case the coherence is essential for the directed transport to persist. In this context it is also appropriate to briefly discuss the influence of internal vibrations of the monomers as they are present e.g. in aggregates of organic dyes[34]. We have performed preliminary calculations to obtain a feeling how the directionality is affected by these vibrations. For a single undamped vibrational mode per monomer, we used the formalism of Ref.[13] which is based on the "coherent exciton scattering" approximation which allows to treat chains up to hundred monomers. We found that the inclusion of a single vibrational mode per monomer barely alters the degree of directionality compared to the purely electronic case of Section IV A. However, similar to the findings in Ref.[13] the velocity of propagation is slowed down. To assess the influence of many (damped) vibra-
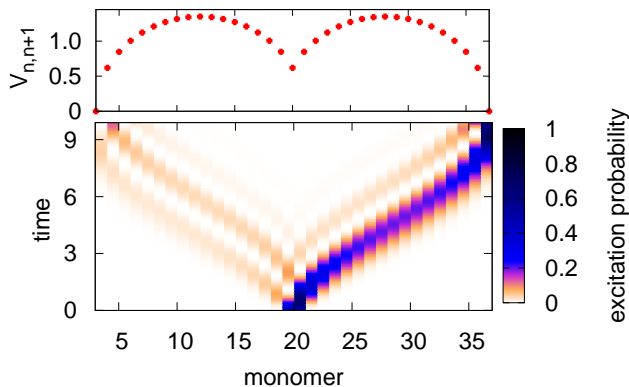
FIG. 3: Engineered interaction between the monomers.
a) Strength of the interaction between monomer n and $n+1$.
b) Corresponding transfer for an initial state with $\Theta = -\pi/2$.

tional modes we used the non-Markovian Quantum State Diffusion (NMQSD) approach of Ref.[25], which allows to treat continuous spectral densities. For a Markovian environment the NMQSD approach can be shown to be equivalent to the master equation (7). Considering environments that are no longer Markovian (e.g. weakly damped vibrational modes) the resulting transfer has a complicated behavior showing both dephasing as well as the influence of individual vibrational modes, which requires further investigations. However, our investigations indicate that the inclusion of vibrational modes does not substantially alter the results found in the present article.

Note that for initial states that consist of coherent superpositions of a large number of monomers a better directionality is possible. For example, we found that when the excitation is delocalised over four monomers the directionality can already exceed 90%. Clearly, when the number of monomers that initially are excited coherently becomes even larger a nearly perfect directionality is possible, e.g. for a Gaussian distribution of k values around a certain mean wave vector k_0 (this results in a Gaussian wave packet in n-space). The present study shows, that even for the smallest possible superposition (involving excitation of only two monomers) pronounced directionality is possible. In this regard it is noteworthy that the directed transfer also works for arrangements where the interaction between neighboring monomers is no longer equal. In nature this is the case e.g. in the LH2 complex of purple bacteria. In artificial systems one might design the couplings (e.g. by changing the distance or orientations between the monomers) such that the propagating wave packet has certain properties like a minimal spread over the monomers or the refocusing at a certain monomer. That such tailoring of the aggregate properties can be combined with the directionality induced by the initial phase is exemplarily shown in Fig. 3 for nearest neighbor interactions as given in panel (a)[37], chosen such that the initial excitation is focused at the end points of the chain. This might stimulate new ideas how to employ the excitonic phase in molecular devices. The directionality imposed by the relative phase in coherent superpositions of localized states might even play a role in the energy transfer in natural light harvesting systems[35], when partly delocalized excitations "hop" from one complex to the next and the exciton remains delocalized over a small number of monomers.

[1] K. Hoki, M. Yamaki, S. Koseki, and Y. Fujimura, J. Chem. Phys. **119**, 12393 (2003).
[2] P. Marquetand, S. Gräfe, D. Scheidel, and V. Engel, J. Chem. Phys. **124**, 054325 (2006).
[3] G. Pérez-Hernández, A. Pelzer, L. González, and T. Seideman, New Journal of Physics **12**, 075007 (2010).
[4] R. E. Merrifield, J. Chem. Phys. **28**, 647 (1958).
[5] W. Goad, J. Chem. Phys. **38**, 1245 (1963).
[6] M. Grover and R. Silbey, J. Chem. Phys. **54**, 4843 (1971).
[7] A. Davydov, *Theory of Molecular Excitons* (McGraw-Hill, 1962).
[8] F. Hofelich, Z. Phys. B **5**, 208 (1966).
[9] H. Haken and P. Reineker, Z. Phys. **249**, 253 (1971).
[10] H. Haken and G. Strobl, Z. Phys. **262**, 135 (1973).
[11] R. J. Silbey and J. Cao, J. Phys. Chem. A **113**, 13825 (2009).
[12] P. Rebentrost, M. Mohseni, I. Kassal, S. Lloyd, and A. Aspuru-Guzik, New Journal of Physics **11**, 033003 (2009).
[13] J. Roden, G. Schulz, A. Eisfeld, and J. Briggs, J. Chem. Phys. **131**, 044909 (2009).
[14] T. Kobayashi, ed., *J-Aggregates* (World Scientific, 1996).
[15] M. Schwoerer and H. Wolf, *Organic Molecular Solids* (Wiley-VCH, 2006).
[16] H. van Amerongen, L. Valkunas, and R. van Grondelle, *Photosynthetic Excitons* (World Scientific, Singapore, 2000).
[17] S. Wüster, C. Ates, A. Eisfeld, and J. M. Rost, Phys. Rev. Lett. **105**, 053004 (2010).
[18] O. Mülken, A. Blumen, T. Amthor, C. Giese, M. Reetz-Lamour, and M. Weidemüller, Phys. Rev. Lett. **99**, 090601 (2007).
[19] F. Robicheaux, J. V. Hernández, T. Topçu, and L. D. Noordam, Phys. Rev. A **70**, 042703 (2004).

[20] J. Frenkel, Phys. Rev. **37**, 17 (1931).

[21] J. Frenkel, Zeitschrift für Physik A **59**, 198 (1930).

[22] J. Franck and E. Teller, J. Chem. Phys. **6**, 861 (1938).

[23] J. L. Magee and K. Funabashi, J. Chem. Phys. **34**, 1715 (1961).

[24] A. Bierman, J. Chem. Phys. **46**, 1484 (1967).

[25] J. Roden, A. Eisfeld, W. Wolff, and W. T. Strunz, Phys. Rev. Lett. **103**, 058301 (2009).

[26] S. Jang, J. Chem. Phys. **131**, 164101 (2009).

[27] D. M. Eisele, J. Knoester, S. Kirstein, J. P. Rabe, and D. A. Vanden Bout, Nature Nanotechnology **4**, 658 (2009).

[28] E. Urban, T. A. Johnson, T. Henage, L. Isenhower, D. D. Yavuz, T. G. Walker, and M. Saffman, Nat. Phys. **5**, 110 (2009).

[29] A. Gaëtan, Y. Miroshnychenko, T. Wilk, A. Chotia, M. Viteau, D. Comparat, P. Pillet, A. Browaeys, and P. Grangier, Nat. Phys. **5**, 115 (2009).

[30] V. May and O. Kühn, *Charge and Energy Transfer Dynamics in Molecular Systems* (WILEY-VCH, 2000).

[31] P. Rebentrost, R. Chakraborty, and A. Aspuru-Guzik, J. Chem. Phys. **131**, 184102 (2009).

[32] P. Reineker and V. M. Krenke, *Exciton Dynamics in Molecular Crystals and Aggregates*, vol. 94 of *Springer Tracts in modern Physics* (Springer Verlag, 1982).

[33] M. B. Plenio and S. F. Huelga, New Journal of Physics **10**, 113019 (2008).

[34] A. Eisfeld and J. S. Briggs, Chem. Phys. **324**, 376 (2006).

[35] V. I. Novoderezhkin and A. P. Razjivin, Chem. Phys. **211**, 203 (1996).

[36] M. Christandl, N. Datta, A. Ekert, and A. J. Landahl, Phys. Rev. Lett. **92**, 187902 (2004).

[37] The interactions on each half are chosen in a way as discussed e.g. in Ref[36].